Nineteenth Symposium (International) on Combustion/The Combustion Institute, 1982/pp. 1321–1329

PARAMETERS INFLUENCING THE EVOLUTION AND OXIDATION OF SULFUR IN SUSPENSION PHASE COAL COMBUSTION

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Stoker coal-fired boiler furnaces are significant in terms of coal consumption and environmental impact; however, they have received relatively little research attention. This paper describes the results of a two-year study on the formation of sulfur oxides in the suspension phase of a coal-fired spreader-stoker system. An eight foot, drop-tube furnace with upward hot-gas flow was used to define the evolution and oxidation of fuel sulfur in the suspension phase and to establish the influence of the combustion parameters on SO_2 formation.

The results indicate that coal particles greater than approximately 0.1 inch fall to the stoker grate essentially unreacted. Thus, only between 8 and 20 percent of the coal feed actually burns in the suspension phase. In general, the evolution and oxidation of sulfur lags hydrogen but leads carbon. The behavior of the organic sulfur closely follows that of carbon; however, the decomposition of the sulfate sulfur depends primarily on the local temperature and oxygen concentration. The behavior of the sulfate sulfur is of major importance because of the high sulfate content of the natural coal fines.

Introduction

The spreader-stoker is the most common large mechanical stoker[1] because it can burn a wide variety of fuels and follow rapid load swings. In this system a multi-blade, overthrow rotor projects large particles (80% > 8 mesh, max size = 1–1/4 inches) onto a moving or vibrating grate. The smaller particles burn in suspension while the heavier pieces fall to the grate for combustion in a thin fuel bed. Coal heat release rates are usually between 500,000 and 750,000 Btu/hr/ft.[2]

The information on sulfur oxidation and control in these systems is very limited. Coal sulfur is generally divided into three groups:[2] sulfate sulfur, pyritic sulfur, and organic sulfur. The available inert pyrolysis data show that the organic sulfur is more volatile than coal carbon or nitrogen but less volatile than oxygen or hydrogen[3,4] and that the inorganic sulfur can interact with the organic matrix.[2,3]

Limestone addition appears to be the most attractive method of SO_2 control in a stoker-fired system. This process involves the calcination of $CaCO_3$ and subsequent reaction to form calcium sulfate.[5] Fundamental and pilot-scale data[6–9] have indicated the viability of the concept and demonstrated the importance of particle size and thermal environment. Recent results[10,11] have emphasized the importance of the carbon chemistry and the local stoichiometry.

This paper summarizes an EPA-funded program to study the evolution and formation of SO_2 in the suspension phase of a coal-fired spreader-stoker. The approach was primarily experimental; a 215,000 Btu/hr, down-fired tunnel furnace was utilized to define the fate of the fuel sulfur under a variety of combustion conditions. Gas and solid-

phase measurements were made at the top and at the bottom of the reactor with three bituminous coals.

Experimental Methods

Tower Furnace

The experimental furnace (Fig. 1) was designed to simulate the environment in the suspension-burning phase of a spreader-stoker. The vertical combustion chamber is 8 feet high with an inside diameter of 6 inches. The main 215,000 Btu/hr natural-gas-fired burner, attached to the horizontal extension at the bottom of the furnace, produced hot combustion products which flowed vertically upward to simulate combustion products leaving an actual stoker bed.

Two 100,000 Btu/hr, natural-gas auxiliary burners, attached to the furnace sides, maintained a constant wall temperature by firing natural gas into the annular channels around the main combustion chamber.

Coal particles were metered with a vibrating-bin, single-screw feeder and transported to a vibrating, water-cooled stainless steel injector located 32 inches from the furnace bottom. The particles falling to the furnace bottom were collected in a water-quenched trap containing six spray nozzles. Unburned particles reaching the flue were collected in a water-quenched, 200-mesh screen basket.

Analytical Measurements

The exhaust SO_2 sample was withdrawn through an uncooled, quartz-lined, stainless-steel probe and measured with a Dupont U.V. 400 Photometric Analyzer. Sample conditioning consisted of glass-wool and stainless-steel filters, an Eaton electrically heated line (maintains sample at 250° F), and two Perma-Pure dryers. Combustion products were also analyzed with a chemiluminescent NO analyzer, a paramagnetic O_2 analyzer, and an NDIR analyzer for CO and CO_2.

The raw coal and solids obtained from either the bottom or exhaust collection systems were analyzed for carbon, nitrogen, and hydrogen with a Perkin-Elmer 240-B elemental analyzer. A Fisher Model 475 sulfur analyzer was used for total sulfur determination; organic, sulfate, and pyritic sulfur were measured by wet chemistry (ASTM D2492).

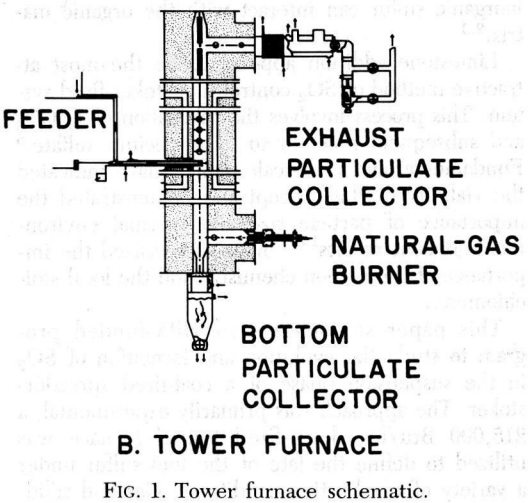

FIG. 1. Tower furnace schematic.

Fuel

Three coal-particle size ranges: 0.0–.063, 0.63–.111, and .111–.157 inches were used. Together they encompass 20 percent of a typical industrial distribution. Both total sulfur content and sulfur forms varied with particle size (Fig. 2). The "natural" coal fines, obtained by mechanically screening the full distribution of stoker-sized coal are rich in sulfate sulfur relative to the overall coal.

Complete analyses of the Indiana, Illinois, and Virginia coals (0.0–0.63 inches) are given in Table 1. These high-volatile bituminous coals were selected because of approximately equal pyritic sulfur contents and variations in total sulfur content and organic/sulfate sulfur ratio.

Experimental Procedure

During the first ten minutes of a typical 30-minute run, the natural gas combustion products were analyzed to establish the gaseous species base-line (without coal). During the remaining 20 minutes coal was injected (ca. 2.0 lb/hr). Subsequently, the coal feed was terminated, and the gas species were allowed to return to base-line values.

Fate of Major Constituents

Figures 3 and 4 present typical results from gas phase analysis for CO, CO_2, and SO_2 and from mass and composition of the solids collected at the furnace top and bottom. (H_2O was estimated by differential hydrogen balance.) The data shown are for the 1900° F thermal condition (wall temperature = 1900° F), the Indiana coal, the smallest 10 percent of a commercial stoker feed ($d < .063$ inches), and a natural gas firing rate equivalent to a bed-heat release rate of 670,000 Btu/hr/ft.^{2} (Commercial practice ranges from 500,000 to 750,000 Btu/hr/ft.^{2})

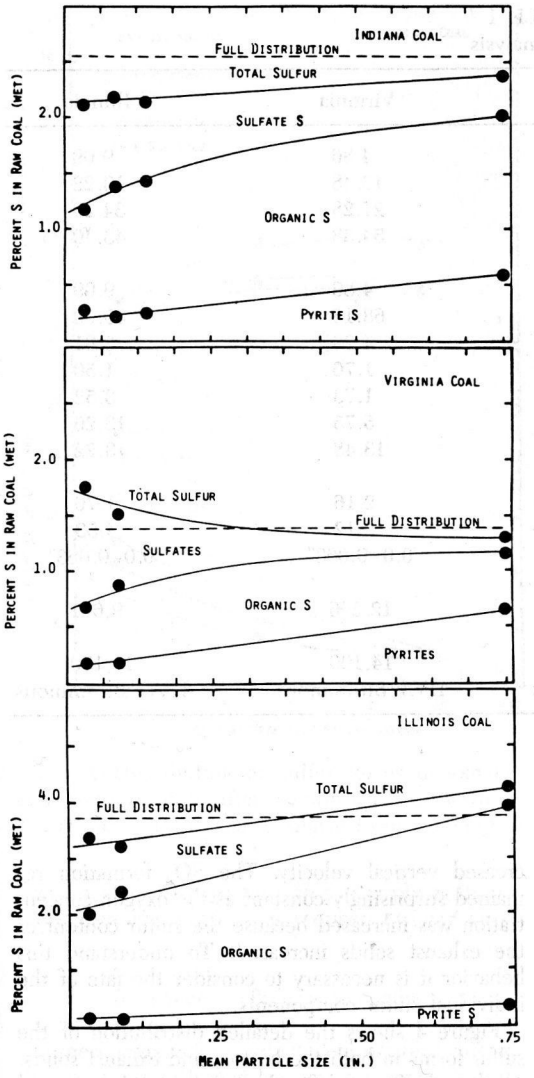

FIG. 2. Influence of raw coal particle size on distribution of sulfur forms for coal studies.

Carbon

Figure 3 indicates that for the smallest particle size range, more than 50 percent of the inlet carbon was oxidized at all conditions. The data are reported in terms of mean free-stream oxygen, the average oxygen concentration in the furnace. (The range was approximately $\pm 1\%$ O_2.) Increasing the mean free-stream oxygen from 2 to 10 percent increased the vertical velocity from 11 to 19 feet per second and decreased the material collected at the furnace bottom (the particles which would fall to the grate in a commercial system) because of increased entrainment. CO_2 formation increased with increasing oxygen due to both increasing entrainment and increasing oxygen partial pressure. Both effects must have been significant because the increase in CO_2 greatly exceeded the decrease in bottom carbon (Fig. 3).

The overall carbon balance was excellent at high mean free-stream oxygen levels, but at low oxygen concentrations approximately 20 percent of the carbon was not accounted for, probably due to the formation of carbonaceous soot which was not collected by the 200-mesh (88 microns) screen system.

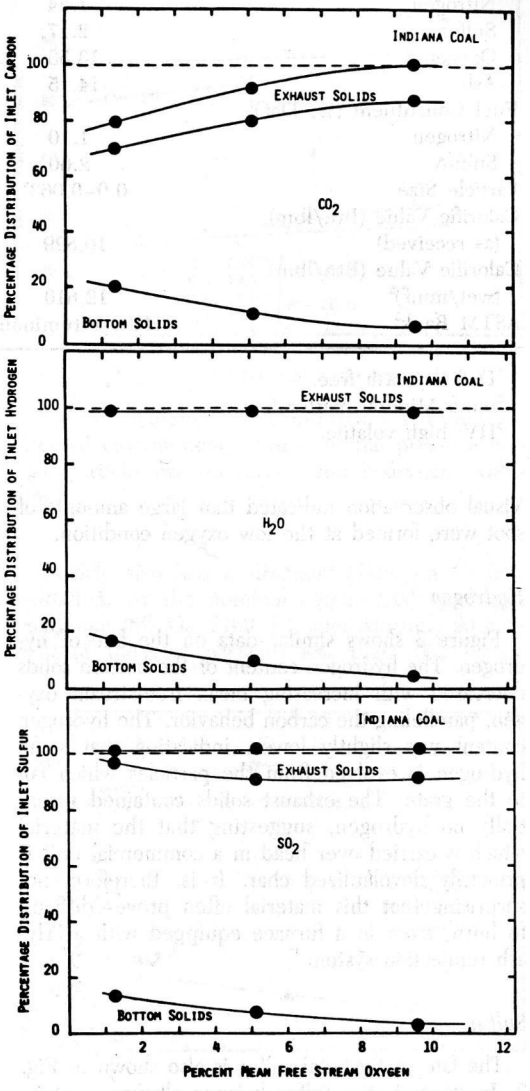

FIG. 3. Fate of carbon, hydrogen and sulfur in the tower furnace for particles <.063 inches in a 1900° F thermal environment and a 670,000 Btu/hr/ft² SRHRR.

TABLE 1
Fuel analysis

Proximate analysis	Indiana	Virginia	Illinois
Moisture	2.96	4.86	9.09
Ash	14.15	13.48	13.22
Volatile Matter	33.45	27.28	34.29
Fixed Carbon	49.44	54.38	43.40
Ultimate Analysis			
Moisture	2.96	4.86	9.09
Carbon	61.79	68.16	55.60
Hydrogen	4.16	4.26	3.81
Nitrogen	1.24	1.76	1.50
Sulfur	2.17	1.73	3.52
Oxygen	13.53	5.75	13.26
Ash	14.15	13.48	13.22
Fuel Constituent (%, Daf)[1]			
Nitrogen	1.10	2.16	1.76
Sulfur	2.60	2.12	4.53
Particle Size	0.0–0.063″	0.0–0.063″	0.0–0.063″
Calorific Value (Btu/lbm) (as received)	10,829	12,206	9,681
Calorific Value (Btu/lbm) (wet/mmf)[2]	12,610	14,100	11,150
ASTM Rank[3]	HVC Bituminous	HVA Bituminous	HVC Bituminous

[1]Daf: dry, ash free.
[2]mmf: Mineral matter free.
[3]HV: high volatile.

Visual observation indicated that large amounts of soot were formed at the low oxygen condition.

Hydrogen

Figure 3 shows similar data on the fate of hydrogen. The hydrogen content of the bottom solids decreased with increasing mean free-stream oxygen, paralleling the carbon behavior. The hydrogen content was slightly lower, indicating that some hydrogen is evolved from the particles which fall to the grate. The exhaust solids contained essentially no hydrogen, suggesting that the material which is carried over head in a commercial unit is primarily devolatilized char. It is, therefore, not surprising that this material often proves difficult to burn, even in a furnace equipped with a "fly-ash reinjection system."

Sulfur

The fate of the total sulfur is also shown in Fig. 3. In general, the sulfur balance closure was significantly better than that achieved with carbon. The sulfur content of the bottom solids decreased with increasing mean free-stream oxygen, a direct result of increased entrainment due to the increased vertical velocity. The SO_2 formation remained surprisingly constant as the oxygen concentration was increased because the sulfur content of the exhaust solids increased. To understand this behavior it is necessary to consider the fate of the individual sulfur components.

Figure 4 shows the detailed distribution of the sulfur forms in both the bottom and exhaust solids. All three sulfur forms in the bottom solid decreased with increasing mean free-stream oxygen due to the increased entrainment. In the raw Indiana coal, the organic sulfur and the sulfate sulfur were approximately equal (Table 1); however, in the bottom solids, the sulfate sulfur was significantly less than the organic sulfur.

Figure 4 also indicates that all forms of the sulfur in the exhaust solids increased with increasing mean free stream oxygen; however, the increase in the sulfate sulfur was unexpectedly dramatic. Increasing the oxygen concentration from 2 to 10 percent increased the exhaust carbon by 100 percent and the organic sulfur by 125 percent, confirming that organic sulfur follows carbon evolution. However, the sulfate sulfur increased by more than 230 percent. Sulfate components are particularly easily decomposed at low oxygen levels; equilibrium calculations for metal sulfates suggest that the 50 percent

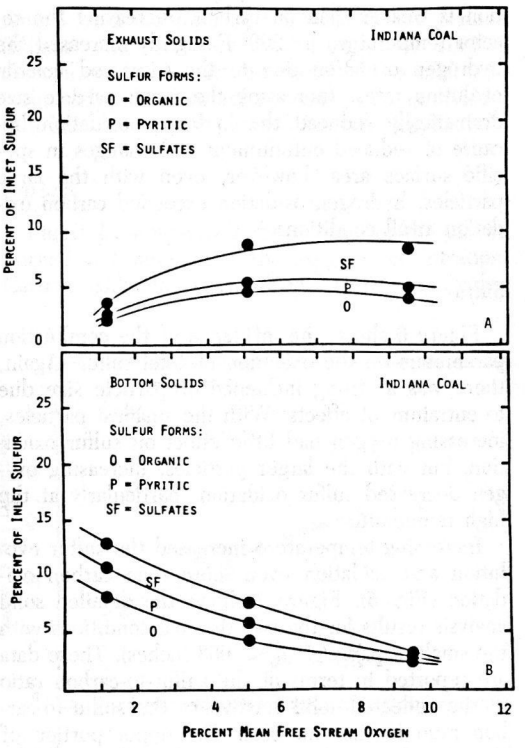

FIG. 4. Distribution of sulfur forms in exhaust and bottom solids after combustion of particles <.063 inches in a 1900° F thermal environment.

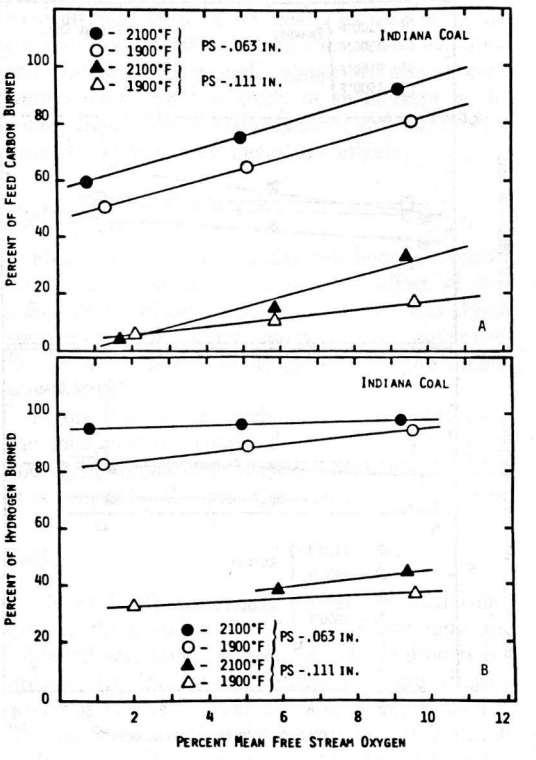

FIG. 5. Influence of combustion parameters; thermal environment, oxygen partial pressure and coal particle size on carbon and hydrogen evolution.

decomposition temperature drops sharply as the local oxygen concentration is reduced to near zero.

Influence of Process Variables

Experiments were conducted to establish the influence of mean free-stream oxygen concentration, particle size, and thermal environment on the fate of carbon, hydrogen, and sulfur in the suspension phase (Figs. 5–7). Reactor wall temperatures of 1900° F and 2100° F, and particle size ranges obtained by mechanically screening the raw coal were studied.

Carbon

Figure 5 summarizes the influence of the combustion parameters on the fraction of the feed carbon oxidized to CO_2 in the suspension phase. Increasing mean free-stream oxygen from 2 to 10 percent increased the carbon oxidized at all combustion conditions studied due to the five-fold increase in oxygen partial pressure and to the increased entrainment caused by the higher vertical velocity.

Particle size had a dramatic effect on Carbon oxidation. At the nominal commercial operating conditions (6% O_2, 2100° F), approximately 80 percent of the coal particles less than .063 inches

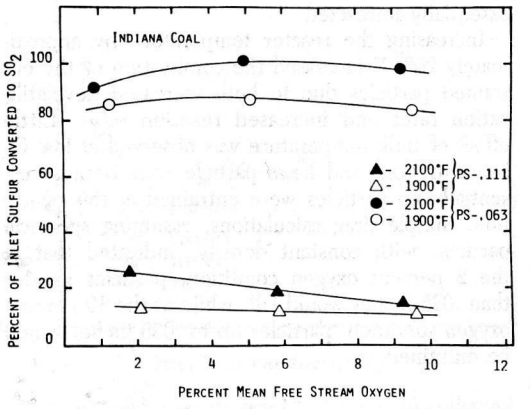

FIG. 6. Influence of combustion parameters; thermal environment, oxygen partial pressure, and particle size on oxidation of total sulfur.

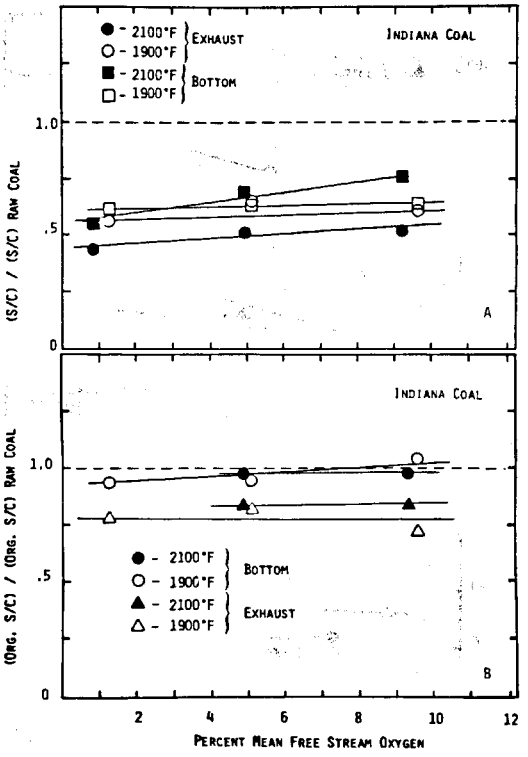

FIG. 7. Solid analysis results of material collected in the bottom and exhaust solid collectors after combustion of particles <.063 inches.

burned in the suspension phase, while less than 20 percent of the particles between .063 and .111 inches burned. Thus, the data shown in Figure 5 indicate that particles small enough to be entrained in the upward flow (less than .063 inches) oxidized almost completely; but large particles which fell directly to the grate ($d > .11$ inches) remained essentially unreacted.

Increasing the reactor temperature by approximately 200° F increased the combustion of the entrained particles due to both increased devolatilization rates and increased reaction rates. Little effect of bulk temperature was observed at low O_2 concentrations and large particle sizes because essentially no particles were entrained at this condition. Simple drag calculations, assuming spherical particles with constant density, indicated that at the 2 percent oxygen condition, particles greater than .025 inches would fall, while at the 10 percent oxygen condition, particles up to .035 inches would be entrained.

Hydrogen

Figure 5 shows that, in general, the influence of the combustion parameters on hydrogen oxidation is weaker than on carbon. Increasing the reactor temperature by 200° F slightly increased the hydrogen oxidation due to the increased volatile evolution rates. Increasing the mean particle size dramatically reduced the hydrogen oxidation because of reduced entrainment and changes in specific surface area; however, even with the large particles, hydrogen oxidation exceeded carbon oxidation at all conditions.

Sulfur

Figure 6 shows the influence of the combustion parameters on the oxidation of total sulfur. Again, there was a strong influence of particle size due to entrainment effects. With the smallest particles, increasing oxygen had little effect on sulfur oxidation; but with the larger particles, increasing oxygen decreased sulfur oxidation, particularly at the high temperature.

Increasing temperature increased the sulfur evolution and oxidation even more than carbon oxidation (Fig. 5). Figure 7 shows the detailed solid analysis results for the two thermal conditions with the smallest particles ($d < .063$ inches). These data are reported in terms of the sulfur-to-carbon ratio in the collected solid relative to the sulfur-to-carbon ratio in the raw coal. The upper portion of Fig. 7 indicates that, in general, sulfur oxidation exceeds carbon oxidation (ratios less than 1.0). Increasing the bulk temperature by 200° F had little influence on the sulfur to carbon ratio in the bottom solids; however, it consistently decreased the sulfur-to-carbon ratio in the exhaust solids (i.e., high temperatures enhance sulfur evolution and oxidation). Figure 7b (lower graph) shows the ratio for the organic components of the sulfur only. These data are much closer to 1.0 and again indicate that, as expected, the organic sulfur follows the carbon. Further, increasing temperature had essentially no effect on this ratio. (It increased both the carbon and organic sulfur evolution by the same amount.) Thus, since increasing temperature significantly reduced the relative total sulfur content of the exhaust solids (Fig. 7a) but had little effect on the organic sulfur (Fig. 7b), it must have significantly increased the decomposition of the sulfate sulfur.

Role of Fuel Composition

Tests similar to those described in the previous sections of this paper were conducted with two other high-volatile bituminous coals in addition to the Indiana coal (Table 1). The sulfur content of the three fuels (smallest particle size) ranged from 1.73 percent (Virginia) to 3.52 percent (Illinois). The pyritic sulfur content of all three fuels was 0.16 ± 0.02 percent, but the organic/sulfate ratio

ranged from 0.5 percent (Virginia) to 1.4 percent (Illinois). All tests were conducted at the 2100° F thermal condition, with the particles less than 0.63 inch, and with a natural gas firing rate equivalent to a bed heat-release rate of 590,000 Btu/hr/ft.[2]

Carbon

Figure 8a summarizes the percent of the carbon burned as a function of the oxygen concentration. Carbon oxidation increased with increasing oxygen concentration for all three coals. As expected, coal composition has influence on the carbon evolution and oxidation. Three high-volatile bituminous coals were selected for this study in an attempt to decouple the effects of sulfur content and distribution from the hydrocarbon chemistry effects.

Hydrogen

Figure 8b also summarizes the hydrogen oxidation results and again shows little effect of fuel composition. In each case the hydrogen was almost completely evolved and oxidized, even under conditions when less than 40 percent of the carbon was oxidized.

Figure 9 shows the carbon to hydrogen ratios in the solid material collected at the furnace bottom and again emphasizes that some devolatilization occurs even with the particles that fall to the grate.

Sulfur

Figure 8c illustrates the fate of the total sulfur for the three coals. Overall, sulfur evolution and oxidation was found to be less than hydrogen but greater than carbon (and nitrogen,[12] not shown), which agrees with previous inert pyrolysis data.[3,4] The sulfur evolution and oxidation was surprisingly similar for all fuels in spite of the large variations in both total sulfur content and sulfur distribution. Further, the dependence on mean free stream oxygen was exactly opposite that observed with carbon (Figure 8a); increasing the mean free oxygen content decreased the SO_2 emissions. Solids analysis data (like that shown in Fig. 4a for the Indiana coal) suggested that this difference was due partly to the reduced stability of the metal sulfates at low

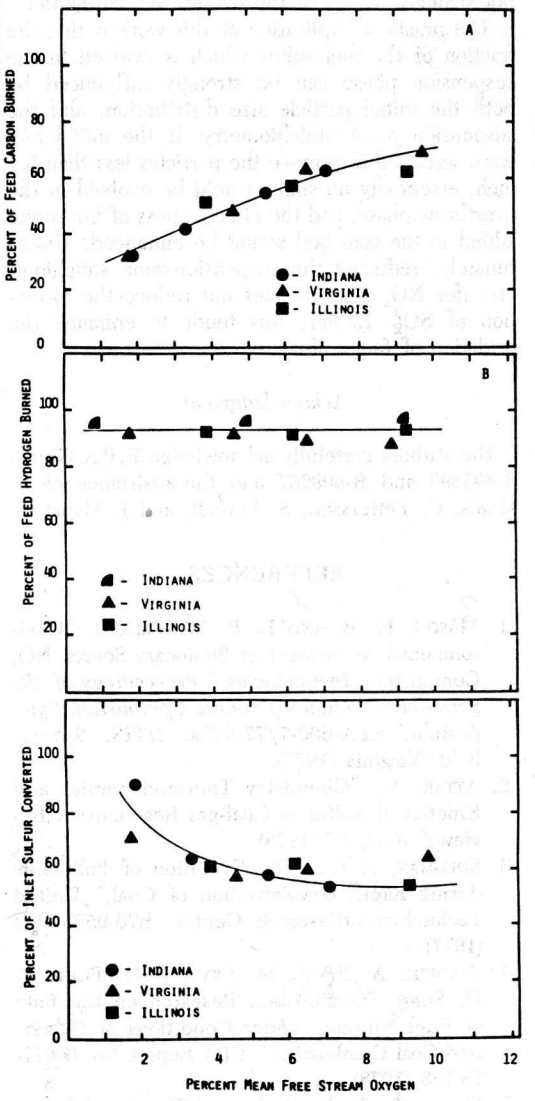

FIG. 8. The influence of oxygen-concentration on carbon, hydrogen, and sulfur evolution and oxidation for particles <.063 inches, in a 2100° F thermal environment at 590,000 Btu/hr/ft² SBHRR.

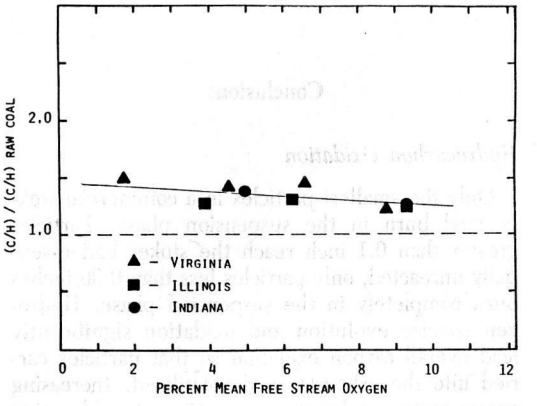

FIG. 9. Solid analysis results of material collected in the bottom collector after combustion of particles <.063 inches in a 2100° F thermal environment.

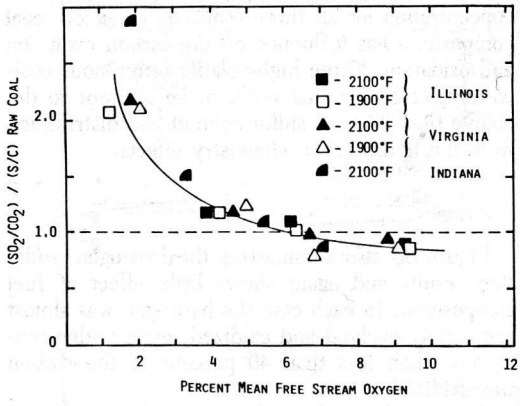

FIG. 10. Influence of oxygen partial pressure on sulfur and carbon oxidation for particles <.063 inches.

oxygen concentrations. Thus, the amount of the organic sulfur which is oxidized depends primarily on the overall coal oxidation rate, while the rate of inorganic sulfur decomposition depends primarily on the local temperature and the local oxygen concentration.

Figure 10 further emphasizes the importance of this effect by presenting these results in terms of the dimensionless SO_2/CO_2 ratio normalized with respect to the sulfur-to-carbon content of the original coal. This figure includes the data for all three fuels, for both thermal conditions and for particles less than .063 inch. When the oxygen availability is limited (low oxygen partial pressures), sulfur will be oxidized preferentially to carbon, and this effect can be relatively large (two fold); but, when oxygen is in great excess, the carbon oxidation may even lead sulfur oxidation slightly.

Conclusions

Hydrocarbon Oxidation

Only the smallest particles in a commercial stoker feed burn in the suspension phase. Particles greater than 0.1 inch reach the stoker bed essentially unreacted; only particles less than 0.06 inches burn completely in the suspension phase. Hydrogen species evolution and oxidation significantly lead overall carbon oxidation so that particles carried into the exhaust are devolatilized. Increasing excess oxygen enhances suspension phase burning due to increased particle entrainment and increased oxygen partial pressure. Increasing the bulk gas temperature also increases both the carbon and hydrogen oxidation.

Sulfur Oxidation

The initial sulfur distribution in the raw coal varies with particle size; naturally occurring fines are unusually high in sulfate sulfur. The evolution and oxidation of organic sulfur depends primarily on the rate of carbon evolution; however, the rate of sulfate sulfur decomposition is most strongly influenced by local oxygen concentration and temperature. At low oxygen levels, sulfur evolution significantly leads carbon oxidation due to the decreased thermal stability of metal sulfates at low oxygen partial pressures. The initial sulfur distribution does not strongly influence the overall SO_2 formation.

The practical implication of this work is that the fraction of the fuel sulfur which is evolved in the suspension phase can be strongly influenced by both the initial particle size distribution, and the suspension phase stoichiometry. If the initial fuel were screened to remove the particles less than 0.1 inch, essentially no sulfur would be evolved in the overthrow phase; and the effectiveness of limestone added to the coal bed would be enhanced. Unfortunately, reducing the suspension-zone stoichiometry (for NO_x control) does not reduce the formation of SO_2. Rather, this tends to enhance the oxidation of fuel sulfur.

Acknowledgment

The authors gratefully acknowledge E.P.A Grants R-805899 and R-809267 and the assistance of S. Manis, C. Pettersson, S. Purcell, and J. Slama.

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